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(54) **PREPARATION OF CATHODE MATERIAL FOR LITHIUM BATTERY**

(57)Abstract:
PROBLEM TO BE SOLVED: To obtain a cathode material having low reactivity with an electrolytic solution and an excellent electric discharge characteristic by adding an org. solvent to a separated carbon core material and washingdrying and calciningafter immersing the carbon core material in a carbon material for coating film formation.
SOLUTION: Washing of a carbon core material with an org. solvent is preferably carried out at 10-300°Cafter immersing the carbon core material in a coating film forming carbon material at 10-300°C. The coating film forming carbon material is a coal and/or petroleum heavy oilsuitably a tar and/or a pitchwhich is preferably made to have primary QI of ≤3% by removing previously at least a part of the primary QI. The org. solvent for washing is selected from toluenequinolineacetone or the likea coal oil and a petroleum oil. Coating ratio (c) of the coating film forming carbon material/(core material + the coating film forming material) is preferably $0<c\leq 0.3$. Spherical particles of which the

corner becomes round are obtained without pulverizing because inter particle fusion and aggregation do not occur even if carrying out washingdrying and calcining.

CLAIMS

[Claim(s)]
[Claim 1]A manufacturing method of a coating carbon material which has an enveloping layer on the surface adding and washing an organic solvent to a separated core material carbon materialand drying and calcinating it to it after a core material carbon material is immersed in a carbon material for covering formation.
[Claim 2]A manufacturing method of a carbon material which has an enveloping layer on the surface adding and washing an organic solvent to a separated core material carbon materialand drying and calcinating it to it after a core material carbon material is immersed in a carbon material for covering formation at 10-300 **.
[Claim 3]A manufacturing method of the coating carbon material according to claim 1 or 2 which adds an organic solvent to a separated core material carbon materialand is washed at 10-300 **.
[Claim 4]A manufacturing method of the coating carbon material according to any one of claims 1 to 3 which immerses in a carbon material for covering formation under decompression of a core material carbon material.
[Claim 5]A manufacturing method of the coating carbon material according to any one of claims 1 to 4 whose carbon materials for covering formation are a Carboniferous system and/or petroleum system heavy oil.
[Claim 6]A manufacturing method of the coating carbon material according to any one of claims 1 to 5 whose carbon materials for covering formation are tar and/or a pitch.
[Claim 7]A manufacturing method of the coating carbon material according to any one of claims 1 to 6 whose organic solvent used for washing is at least one sort chosen from toluenequinolineacetonehexanebenzenexylenemethylnaphthalenealcoholsa Carboniferous system oiland a petroleum system oil.
[Claim 8]A manufacturing method of the coating carbon material according to any one of claims 1 to 7 a range of whose rate of solid content at the time of washing and an organic solvent is 1:0.1-10 in a weight ratio.
[Claim 9]A manufacturing method of the coating carbon material according to any one of claims 1 to 8 whose covering ratio (c) defined as a weight ratio of carbon material/for covering formation (carbon material for core material + covering formation) is 0< c<=0.3.
[Claim 10]A manufacturing method of the coating carbon material according to any one of claims 1 to 9 in which a carbon material for covering formation removes at least a part of primary QI beforehandand makes primary QI 3% or less.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
Work A carbon materialits manufacturing methodespecially the surface more way part Nomoto invention about the end of carbon powder it was covered with ingredientssuch as

heavy oiland its manufacturing method in details. An isotropic graphite material raw materiala lithium secondary battery negative pole materialetc. are carried outand it is related with a useful carbon materiala manufacturing method for the sameand the lithium secondary battery using such a carbon material.
[0001]Back View A miniaturization and weight saving of portable equipments (henceforth a "portable device")such as an electronic device and information machines and equipmentare advancing splendidlyand the rechargeable battery which drives them is becoming very important parts in recent years [technical]. Since a lithium secondary battery has a light weight and high energy densitypromising ** is carried out as a power supply for a drive of a portable deviceand research and development are furthered actively. Howeverwhen a lithium metal is used for an anodein order that a dendrite may generate and grow and may cause an internal short circuit on metal lithium by repeating a charging and discharging cyclerechargeable-battery-izing is difficult. Although it replaces with a lithium metal and use of a lithium alloy like a lithium aluminum alloy is proposedif a charging and discharging cycle or deep charge and discharge is performed in this casein order that the segregation of an alloyetc. may startcharacteristic sufficient in the long run is not obtained.
[0002]Thena carbon material is used as a host materialthe cell using the anode using the insertion elimination reaction of the lithium ion is proposedand research and development have been furthered and put in practical use. The lithium secondary battery which uses a carbon material for an anode is excellent in a cycle characteristicsafetyetc.
[0003]Howeverwhile a carbon material has a broad structure thru/or form of black lead to amorphous carbonin order that the fine texture which those property values or a carbonaceous hex-steel side forms may influence the performance of an electrode greatlyvarious carbon materials which specified a property value or fine texture are proposed.
[0004]The thing of a carbon system which roughly divided and was calcinated at around 1000 **and the thing of a black lead system calcinated at around 2800 ** are among the negative pole materials for lithium secondary batteries used now. The former has the advantage that there are few reactions with an electrolysis solution and disassembly of an electrolysis solution cannot break out easilywhen it uses as an anode of a lithium secondary batterybut there is a fault that change of the potential accompanying discharge of a lithium ion is large. On the other handthe latter has the advantage that change of the potential accompanying discharge of a lithium ion is smallwhen it uses as an anode of a lithium secondary batterybut. It reacts to an electrolysis solutiondisassembly of an electrolysis solution arisesand there is a fault that a carbon material is destroyed further (J. Electrochem. Soc. 117222 (1970)). As a resultin the latterproblemssuch as decline in charge and discharge efficiencya fall of a cycle characteristicand a safety fall of a cellarise. Since it is reported that the material of a black lead system is also usable when using a specific electrolysis solutionbut (J. Electrochem. Soc. 1372009 (1990)) an electrolysis solution is limitedWhen a cell is producedthere is a problem that the improvement of the temperature characteristics of a cella cycle characteristicetc. is considerably restricted by the kind of electrolysis solution.
[0005]JPH4-368778AJPH4-370662AJPH5-94838AJPH5-121066Aetc. have proposed the carbon material which covered the graphite-grains child's surface with low crystal carbon that this problem should be solved. Since these surface treatment carbon materials press

down disassembly of an electrolysis solutionthey are effective to the increase in cell capacityan improvement of a cycle characteristicetc.
[0006]Howeveraccording to technology given in JPH4-368778Asince the carbon coating layer is formed in the carbon particle surface by the gaseous phase methodweld of each carbon particlecondensationetc. do not take placebut the material which was excellent in the performance is obtainedbut it is fieldssuch as a cost aspect and mass production natureand there is a practically big problem.
[0007]The technique of having used promising liquid phase carbonization for JPH4-370662AJPH5-94838Aand JPH5-121066A from a cost aspect and mass production nature is indicated. Howeverby only mixing and calcinating the organic compound and graphite-grains child of the liquid phase. Since graphite-grains children weld and condense in the case of carbonizationproblemslike that an impurity mixes at the time of grinding which needs to grind material and a field [activity / black lead] newly exposes by grinding in the case of electrode productionand a process becomes still more complicated are produced.
[0008]**. ** In indication this inventionthe anode which there are not selectivity about an electrolysis solution thru/or restrictionsand uses a carbon material with a small electrical change of discharge of a lithium ion is produced.
Thereforeit primarily aims to obtain the lithium secondary battery excellent in various characteristicssuch as cycle nature and safety.

[0009]The result of having inquired wholeheartedly this invention person canceling thru/or reducing the problem of the above conventional technologiesThe particle state carbon material (there is also only the following "core material carbon material" thru/or "carbon material used as a core material"or "core material") used as a core material The raw material for carbon materials for covering formation. When it faced separating this from heavy oil etc. and a specific means was adopted after making it immersed for (for exampleCarboniferous system heavy oilsuch as tar and a pitchor below petroleum system heavy oil; only saying "heavy oil")it found out that a core surface could manufacture the carbon material uniformly covered in the pitch. And the carbon material particles of the two-layer structure acquired by carrying out in this way are carrying out form which spherical thru/or is approximated to the shape of an ellipsoidor it.
It became clear that form where the edge part of the carbon crystal became round was carried out.
As a result of measurement by a BET adsorption methodcompared with the core material carbon material before processingthe value of the specific surface area of particles is smalland the fine pores which participate in the specific surface area by a BET adsorption method became clear [also being closed with a certain style].
[0010]. [whether according to this inventionthe carbon material originating in heavy oil etc. adheres to the edge of a carbon materialand some or all of a basolateral used as a core materialand] Or some or all of edge and a basolateral is covered with this carbon materialand the particle state coating carbon material almost spherical thru/or being an ellipsoid-like is provided. In this carbon materialthe fine pores which participate in the specific surface area measured by a BET adsorption method are closed by the carbonaceous adhesion or covering originating in heavy oil etc.and specific surface area is below $5m^2/g$ (preferably 1-5 m^2/g grade).

[0011]In this inventionthe average spacing (d002) of the field by an X ray wide angle diffraction method (002) as a carbon material used as a core material 0.335-0.340 nm(002) The microcrystal thickness (Lc) of a plane direction uses the high crystalline graphite material whose not less than (preferably not less than 40 nm) 10 nm and microcrystal thickness (La) of a plane direction (110) are not less than (preferably not less than 50 nm) 10 nm.
[0012]In the carbon material by this inventionit is the feature that the degree of crystallinity of the carbon material (henceforth the carbon material for covering formation) which adhered to the core surface or has covered the core surface is low compared with the degree of crystallinity of the above-mentioned core material.
[0013]The value of the true specific gravity of the carbon material by this invention is in the range of 1.50-2.26g / cm^3.
[0014]When adopting such a carbon material as a negative pole material of a lithium secondary batteryit is high capacity and a lithium secondary battery with high safety can be obtained.
[0015]The above coating carbon materials by this invention are manufactured as follows. Firstthe carbon material used as a core material is preferably immersed in heavy oil of Carboniferous systemssuch as tar and a pitchor a petroleum systemetc. at about 10-300 **It driesafter adding an organic solvent to the coating carbon material separated after covering with heavy oil etc. and separating this covering core material carbon material from heavy oil etc. subsequently and washing at about 10-300 ** preferably.
[0016]This invention also provides the manufacturing method of the carbon material which carries out carbonization calcination of the coating carbon material covered with the heavy oil etc. which were produced by performing it aboveand the manufacturing method of the carbon material which carries out graphitization calcination of the coating carbon material covered with the heavy oil produced by performing it above.
[0017]In this inventionit is preferred to make it the particle of 1 micrometer or less by laser diffraction type particle-size-distribution measurement become 10% or less of the whole with the integrated value of a volume reference in the carbon material obtained by the above-mentioned manufacturing method.
[0018]In this inventionit is preferred to use tar or the pitch which removed at least a part of primary QIand primary QI which remains made 3% or less (preferably 1% or less) as heavy oil which immerses a carbon material.
[0019]The anode for lithium secondary batteries using the negative pole material for lithium secondary batterieswherein this invention makes a component above-mentioned carbonization or the charge of a graphitized carbon materialand this negative pole materialthe nonaqueous lithium secondary battery using this anodeand a solid electrolyte secondary cell are provided further.
[0020]When the carbon material which "is [almost spherical or] an ellipsoid-like" in this invention is observed by SEM etc.have inherited the form of the carbon material particles which are core materialsbut. All or the carbon ingredient which originates in a fuel oil etc. in part of the edge of the carbon material which is a core materialand basolaterals adheresand the carbon material in the state where the angle is lost is also included. Although such a carbon material is efficiently manufactured in the manufacturing method of the invention in this application which does not include a crushing step after covering and calcinationIn this invention which is not what is limited to the material produced by

this manufacturing methodThe carbon material in which the fine pores which participate in the specific surface area measured by a BET adsorption method originate in a Carboniferous system or petroleum system heavy oil, such as the raw material for carbon materials for covering formation, i.e., tar, and a pitch, etc. adheres, Or it is covered with such a carbon material and the fine pores which participate in the specific surface area measured by a BET adsorption method include the state where it is selectively closed at least by the fired material (this is called carbon material for covering formation) of the raw material for carbon materials for covering formation, withcarbon material with which it is closed. That isfine pores do not need to be thoroughly buried with the carbon material originating in heavy oil etc.for examplea carbon material adheres only near the entrance of fine poresand the carbon material which has the fine pores with which the entrance was plugged up is also included. Such a state is checked when specific surface area is measured with a BET adsorption methodand specific surface area is small.
[0021]Four combination on the carbon material obtained by this invention and of a low crystal carbon material + low crystal carbon material; low crystal carbon material + quantity crystallinity carbon material; quantity crystallinity carbon material + low crystal carbon material; quantity crystallinity carbon material + quantity crystallinity carbon material is possibleThe effect of reducing disassembly of an electrolysis solutionetc. in all the cases is acquired.
[0022]In this inventionlow crystal carbon means "the carbon which cannot serve as graphite crystals even if it carries out processing (for examplehigh temperature processing) neededsince it graphitizes"and such carbon is usually called hard carbon. High crystallinity carbon means "the carbon which serves as graphite crystals by carrying out processing and processing carried out since it graphitizes"and such carbon is usually called soft carbon.
[0023]the exterior carbon material ("the carbon material for covering formation".) originating in the heavy oil etc. which adhered to the core material and the core materialor have covered the core material in this invention The carbon material which has the following eight kinds of composition is obtained by adjustment of the combination which may be called "the carbon material for surface treatment"covering materialetc.and the last calcination temperature. Namelycarbon material by which ** carbonization processing was carried out and in which a core material consists of a low crystal carbon materialand the carbon material for covering formation consists of a low crystal carbon material;
** Carbon material by which carbonization processing was carried out and in which a core material consists of a low crystal carbon materialand the carbon material for covering formation consists of a high crystallinity carbon material;
** Carbon material by which conducting graphitization treatment was carried out and in which a core material consists of a low crystal carbon materialand the carbon material for covering formation consists of a low crystal carbon material;
** Carbon material by which conducting graphitization treatment was carried out and in which a core material consists of a low crystal carbon materialand the carbon material for covering formation consists of a high crystallinity carbon material;
** Carbon material by which carbonization processing was carried out and in which a core material consists of a high crystallinity carbon materialand the carbon material for covering formation consists of a low crystal carbon material;

** Carbon material by which carbonization processing was carried out and in which a core material consists of a high crystallinity carbon materialand the carbon material for covering formation consists of a high crystallinity carbon material;
** The carbon material by which conducting graphitization treatment was carried out and in which a core material consists of a high crystallinity carbon materialand the carbon material for covering formation consists of a low crystal carbon material; and ** conducting graphitization treatment is the carbon material which was carried out and in which a core material consists of a high crystallinity carbon materialand the carbon material for covering formation consists of a high crystallinity carbon material.
[0024]An exterior carbon material covers a core material in this invention. Thereforespecific surface area is small and the carbon material for rechargeable batteries excellent in charge/discharge capability can be obtained efficiently.
According to the combination of the core material and covering material which are especially shown in above ****and **according to the combination of the core material and covering material which the carbon material for cells which was remarkably excellent in charge/discharge capability is obtainedand are shown in ********and **specific surface area is small and the carbon material for cells which can improve the safety of a cell is obtained.
[0025]In this inventionas a carbon material used as a core materialOne sort of natural graphite of particle state (the shape of a scale thru/or massfibrouswhisker shapea globular shapea granular typeetc.)an artificial graphitemeso carbon micro beadsmesophase pitch powderisotropic pitch powdera resinous coaleach carbonization articleand a graphitization article or two sorts or more can be used. Also in thesesince the shape of a scale thru/or massive natural graphiteand an artificial graphite are dramatically inexpensivethey are preferred from the field of cost. Since the carbonization article and graphitization article of meso carbon micro beads (MCMB) are material with dramatically small specific surface area and material with smaller specific surface area can obtain them when using it as a core materialthey are preferred from the field of the safety of a rechargeable battery.
[0026]As a carbon material used as a core materialstill more preferablyThe average spacing (d002) of the field by an X ray wide angle diffraction method (002) is 0.335-0.340 nmand the microcrystal thickness (Lc) of a plane direction (002) is not less than (preferably) 10 nm. Not less than 40 nm and the microcrystal thickness (La) of a plane direction (110) are not less than (preferably) 10 nm. It is preferred that the peak intensity ratio near 1360cm^{-1} to the peak intensity ratio not less than 50 nm and near [by argon laser Raman] 1580cm^{-1} (it is henceforth described as an R value) is 0.5 (0.4 or less [Preferably]) or less. When an average spacing is larger than 0.340 nmwhen Lc and La are smaller than 10 nmor when an R value exceeds 0.5The crystallinity of a carbon material is not enoughand since the capacity of the low potential portion (it is 0-300 mV at the potential standard of Li) near a dissolution deposit of lithium becomes less enough when a coating carbon material is producedit is not desirable.
[0027]As for the particle size distribution of the carbon material used as a core materialit is preferred that it is about 0.1-150 micrometers. In order to depend for the particle diameter of the ultimate product containing the carbon material for covering formation originating in heavy oil etc. on the particle diameter of the carbon material which is a core material substantiallythe particle diameter of an ultimate product will also be mostly

prescribed by the particle diameter of a core material. When the particle diameter of a core material is smaller than 0.1 micrometerSince the homogeneity of an electrodethe pack density of an active materialthe handlability on the process of producing an electrodeetc. fall in becoming larger than 150 micrometers to the danger of causing an internal short circuit through the hole of the separator of a cell becoming highneither is preferred.

[0028]As for the weight ratio of the carbon material for covering formation originating in heavy oili.e.carbon material/for covering formation(carbon material for core material carbon material + covering formation) (below as for :this ratio is called "covering ratio")it is preferred that it is 0.3 or less more greatly than 0and it is more preferred that it is 0.01-0.2. In this casethe thickness of covering carbon serves as the range of about 0.01-10 micrometersand still more desirable thickness is about 0.05-5 micrometers.

[0029]When the covering ratio exceeded 0.3 and a cell is produced since the capacity in the low voltage portion originating in a core material decreasesit becomes difficult to obtain sufficient capacity. The quantity of covering carbon here is the value which conducted solvent analysis about the carbon ingredient originating in the heavy oil etc. which have covered the circumference of the core material before calcinationand measured the quantity of quinoline soluble. A carbon material is a sphere while the thickness of the carbon material for covering formation measures the diameter of a centriole of the carbon material before covering which serves as a core material with a laser diffraction type particle-size-distribution plan (D50)and the diameter of a centriole of the pitch component coating carbon material before calcination (D50).

It is the value which computed it as {(particle diameter after covering) - (particle diameter of the charge of covering Maehara)}/2 having assumed after calcination that the form of the enveloping layer of a pitch component is maintained.

[0030]In this inventionthe combination whose surface carbon material for covering formation is a low crystal from the carbon material of a core material is preferred. The average spacing (d002) of the field by a wide angle X-ray diffraction method (002) is 0.335-0.340 nmand the microcrystal thickness (Lc) of a plane direction (002) is not less than (preferably) 10 nm. It is preferred that the R value according [not less than 40 nm and the microcrystal thickness (La) of a plane direction (110)] to not less than (preferably not less than 50 nm) 10 nm and argon laser Raman spectroscopy is 0.5 (0.5 to about [Preferably] 1.5) or more. Although a spacing and an R value are the indices of the degree of crystallinity of common black leadby Raman spectroscopythe physical properties of the surface of material are reflected on the character of these measuring methods to the character of bulk being reflected in a property value in an X-ray diffraction method. that isthe material which fulfills the above-mentioned property value -- as the character of bulk -- high -- though it is material [****]it means that the surface is a low crystal. Since surface crystallinity is high when the material R value after calcination is smaller than 0.5the selectivity of a solvent is not lost thoroughly. When the average spacing (d002) which is the character as bulk deviates from the range which is 0.335-0.340 nmchange of the potential accompanying the occlusion and discharge of a lithium ion becomes largeand is not preferred.

[0031]the true density of the coating carbon material of the acquired two-layer structure -- 1.50-2.26g / cm^3 grade -- desirable -- 1.8-2.26g / cm^3 grade -- they are 2.0-2.26g / cm^3

grade more preferably. Since active material density in an electrode cannot be raised when true density produces an electrode using a low materialeven if it is a material excellent in the characteristic per weightit is difficult to obtain the cell of high capacity.
[0032]As for the particle diameter of a coating carbon materialwhat has particle size distribution in the range of 0.1-150 micrometers is preferredand it is still more preferred in this particle size distribution that a particle of 1 micrometer or less is 10% or less in a volume reference. Since a battery characteristic falls according to increase of specific surface area when a particle of 1 micrometer or less exceeds 10% by a volume reference in particle diameterit is not desirable.
[0033]The coating carbon material obtained by this invention carries out metallic mold restoration in the state of powderand after it carries out application-of-pressure moldingit can also obtain the carbon block or graphite block which has a uniform presentation by calcinating.
[0034]As a raw material for carbon materials for covering formationnaphthalenephenanthreneAn acenaphthyleneanthracenetriphenylenepyrenea chryseneAromatic hydrocarbonsuch as perylenethe tar produced by carrying out the polycondensation of these under heat pressingpitches or the tar which uses the mixture of these aromatic hydrocarbon as the main ingredientsa pitchasphaltand oil are raisedand the origin does not ask a petroleum system and a Carboniferous system. In this Descriptionthese raw materials for carbon materials for covering formation may only be called "heavy oil (a petroleum system or a Carboniferous system) etc." Although it becomes disadvantageous in costit is also possible to use various kinds of thermosetting resin as a raw material for covering formation.
[0035]When using Carboniferous system heavy oilit is preferred to use tar or the pitch which removed at least a part of primary QI which exists in a raw materialand made primary QI which remains 3% or less (preferably 1% or less). Primary QI means here the free carbon originally contained in coal tar. If primary QI exists in a raw materialthe fall of the characteristic at the time of checking carbonization in the case of calcinationand mixing into an ultimate product as an about 1-micrometer spherical carbon grain etc. causing the manufacturing process top problem of an electrodeor considering it as an electrode may be caused.
[0036]Usuallyalthough it is a solid at ordinary temperaturesoftening melting of the heavy oil is carried out by heating. This temperature it begins to soften is called softening temperature (SP). In order to specify the quality of heavy oilthe toluene insoluble at the time of usually carrying out solvent judgment by toluene is used. Although these are typical methods of specifying heavy oilin specifying the quality of heavy oilin this inventionarbitrary methods can be chosen suitably.
[0037]In this inventionagitation treatment of a carbon materialheavy oiletc. used as the above-mentioned core material is mixed and carried out. The mechanical agitation method which is not limitedfor exampleuses a ribbon mixera screw type kneaderan omnipotent mixeretc. especially as agitation means is mentioned.
[0038]Although stirring processing conditions (temperature and time) are suitably chosen according to the ingredient of a raw material (a core material and heavy oil for covering)the viscosity of a mixtureetc.they are usually about 10-300 **.
It is more preferred to consider it as the range of about 50-200 ** or to also adjust time collectively so that the viscosity of a mixture may be 5000 or less Pa-s.

Thusit is possible by adjusting the treatment temperature and time at the time of stirring to control the thickness of the enveloping layer (it is also only called an enveloping layer) of the raw material for covering formation. That isby shortening making temperature high and/or timethickness of an enveloping layer can be made small and thickness of an enveloping layer can be enlarged by making temperature low conversely. Since an enveloping layer does not become uniform unless churning is enoughit is not desirable. What is necessary is just to choose mixing time suitablysince mass production nature becomes low and is not preferred practicalwhen too long although it generally does not have an adverse effect on the description of a product.
[0039]Although it may be any under atmospheric pressureapplication of pressureand decompression as an atmosphere at the time of churningsince familiarity by a core material and heavy oil improves in agitating under decompressionit is desirable.
[0040]In this inventionif necessary because of enlarging thickness of an enveloping layer which improves familiarity by the core material and an enveloping layer and which makes thickness of an enveloping layer uniform etc.it is also possible to repeat the above-mentioned mixed stirring process two or more times. A cleaning process may be presented once separating the covered core material in advance of the continuing cleaning process.
[0041]Subsequentlya cleaning process is presented with the coating carbon material covered with the heavy oil etc. which were produced by performing it above. As an organic solvent used for washingtoluenequinolineacetonehexanebenzenexylenemethylnaphthalenealcoholsa Carboniferous system oila petroleum system oiletc. are mentioned. In thesetoluenequinolineacetonebenzenexylenemethanolCarboniferous system gas oil and middle oilpetroleum system gas oilmiddle oiletc. are more preferred. Since the insoluble matter in a washing solvent can newly be given to an enveloping layer when choosing these organic solvents suitablyit is also possible to control the heavy oil ingredient of an enveloping layer.
[0042]Although what is necessary is just to define washing temperature in consideration of the description etc. of the coating carbon material obtained eventuallyespecially its surface coated layer and it is not limited in particularits about 10-300 ** is preferred.
[0043]As for the rate of the solid in the case of washing {= core material + enveloping layer thru/or impregnation layer (it is only considered as an enveloping layer below)}and an organic solventit is preferred that it is the range of 1:0.1-10 in a weight ratio.
[0044]In a cleaning processit is possible by choosing the kind of solventcleaning timewashing temperatureetc. to adjust the thickness of an enveloping layerthe heavy oil ingredient which remainsetc. For examplein combining suitably conditionssuch as using a solvent with a weak detergencyand making washing temperature low to the thickness of an enveloping layer becoming thin about conditionssuch as using a solvent with a strong detergencyand making washing temperature highin combining ****it becomes possible to thicken thickness of an enveloping layer. What is necessary is just to choose cleaning time suitably in consideration of the above-mentioned monograph affair.
[0045]Subsequentlythe partition process of a coating carbon material and an organic solvent is performed by techniquessuch as centrifugal separationan expressionand gravity settling. The temperature at the time of dissociating is usually in the range of about 10-300 **.

[0046]Desiccation of the separated coating carbon material is usually performed in 100-400 **.
[0047]Thusthe obtained dry coating carbon material does not have carbonization treatment and that the pitch component of the circumference of a core material particle is maintainedand particles weld thru/or condense even if it performs conducting graphitization treatment further.
[0048]Subsequentlythe coating carbon material dried above is calcinated. When carbonizing a coating carbon materialit is possible to calcinate at the temperature of about 600-2000 **and it is more preferred to calcinate at the temperature which is about 900-1300 **. When it graphitizesat the temperature of about 2000-3000 **calcinating is possible. It is more preferred to calcinate at the temperature of about 2500-3000 **.
[0049]In order to maintain a low crystalcalcinating at the elevated temperature on carbonization or graphitization conditionsIt is also possible for oxidizing gasessuch as oxygenozonecarbon monoxideand SOxto perform difficulty conducting graphitization treatment in a low-temperature degree region (about 50-400 **)and to calcinate at an elevated temperature after that to the covered heavy oil layerin advance of calcination of a coating carbon material. For exampleafter making the enveloping layer of high crystallinity form in the core material of high crystallinityit is also possible by performing oxidation treatment to change an enveloping layer into low crystal carbon. On the contrarywhen not performing such oxidation treatmentit is also possible to maintain an enveloping layer in the state of high crystallinity. Such oxidation treatment is performed in advance of carbonization calcination of a coating carbon material. In this casethe carbon material obtained is useful as a lithium secondary battery negative electrode material.
[0050]As an atmosphere at the time of calcination of a coating carbon materialnon-oxidizing atmospheressuch as a sealed state of inactive gas and a vacuaare mentioned among reducing atmosphere and an inactive gas air current. Irrespective of calcination temperaturea heating rate is suitably chosen from the range about 1-300 ** / hrand firing time is 6 hours - about one month. Temperature up can also be gradually carried out according to the thickness of an enveloping layeretc.
[0051]When performing vacuum carbonizationit is preferred to continue a reduced pressure state from ordinary temperature to the highest arrival temperatureor to consider it as a reduced pressure state in a suitable temperature region (preferably not less than 500 **). Vacuum carbonization is effective in removing the surface functional group of a coating carbon materialand can reduce the irreversible capacity of a cell.
[0052]Generallyat a late heating rate (below 10 ** / hr)formation of a precise enveloping layer is expectable to improvement in mass production nature being expectable at a quick heating rate. It is possible to take various formssuch as linear temperature up and gradual temperature up which holds temperature with a constant intervalas a temperature profile at the time of temperature up and calcination.
[0053]Since reactivity with the organic solvent of an electrolysis solution is low when the circumference acquired by carrying out such uses the carbon material covered with the carbon material for covering formation as a lithium secondary battery anodeneither disassembly of an electrolysis solution nor destruction of a carbon material takes place easily. As a resultthe charge and discharge efficiency of a cell improvesand it has the advantage that the safety is improved. Generallysince the end face (edge plane) of

activity microcrystal is carrying out orientation of the material of a black lead system outsideit reacts to an electrolysis solution easily. In this inventionthe pitch component in which the basolateral (basal plane) which is carbonaceous condensed multi-ring meshes of a net is carrying out orientation outside has covered this activity microcrystal end face. Thereforeit is thought that a reaction with the organic solvent of an electrolysis solution is controlled.

[0054]The quantity of covering heavy oil of the circumference of a carbon material thru/or the thickness of an enveloping layer are controllable by this invention by adjusting a kinda cleaning condition (timetemperature)etc. of an organic solvent at the time of washing the temperature which immerses the carbon material which is a core material in heavy oil etc.timeor the covered carbon material.
Thereforethe basolateral which is carbonaceous condensed multi-ring meshes of a net can manufacture the carbon material which had the surface covered by the pitch component which is carrying out orientation in the direction of the surface of a carbon material.

[0055]Carbonization or the state where the basolateral carried out orientation in the direction of the surface of a carbon material in covering of a core surface even if graphitized further is maintained in these carbon materials. Thereforesince it is hard to react to the organic solvent of an electrolysis solution in using this carbon material for a lithium secondary battery anodeneither disassembly of an electrolysis solution nor destruction of a carbon material takes place. As a resultthe charge and discharge efficiency of a cell serves as a high valueand the prominent effect of excelling also in the safety of a cell is acquired.
[0056]After presenting processing of distributioncrackinga classificationetc. with the coating carbon material produced by making it above if necessary in producing the lithium secondary battery by the invention in this applicationit adjusts to a suitable particle size and is considered as an electrode material.
[0057]an electrode is publicly known -- a binder -- after mixing An active material layer is formed on a charge collector. Especially as a binderit is not limited but polyolefin system polymer; synthetic rubberssuch as fluorine system polymer; polyethylenesuch as polytetrafluoroethylene and polyvinylidene fluorideand polypropylenecan be used. As a quantity of the binder in this caseit is usually the range of about 3-50 weight sections to active material 100 weight sectionand is about 5-20 weight sections more preferablyand they are about 5-15 weight sections still more preferably. Since the density of the active material in an electrode will fall if there is too much quantity of a binderit is not desirable. Since the capability to hold the active material in an electrode will not be obtained enough but the stability of an electrode will fall if there are too few bindersit is not desirable. The paste which mixed the active material and the binder is produced as a method of forming an electrodeThe method of forming an active material layer on a charge collector by doctor bladea bar coating machineetc. or the method of putting into a molding machine etc. what mixed the active material and the binderand using as a Plastic solid with a press etc. is mentioned.
[0058]As an electrolyte of the lithium secondary battery by the invention in this applicationpublicly known organic electrolysis liquidan inorganic solid electrolytea solid polymer electrolyteetc. can be used.

[0059]Also in thesethe viewpoint of ionic conductivity to especially organic electrolysis liquid is preferred. As a solvent for organic electrolysis liquidpropylene carbonateethylene carbonateButylene carbonatediethyl carbonatedimethyl carbonateEster speciessuch as methylethyl carbonate and gamma-butyrolactone; A tetrahydrofuranSubstitution tetrahydrofuranssuch as 2-methyltetrahydrofuran; DioxolaneEthersuch as diethyletherdimethoxyethanediethoxyethaneand methoxyethoxy ethane; Dimethyl sulfoxideSulfolanemethyl sulfolaneacetonitrilemethyl formatemethyl acetateetc. are illustratedit is independentor these can be mixed and used. As an electrolytelithium perchloratelithium borofluoride6 fluoridation [phosphoric acid] lithiumLithium saltsuch as 6 fluoridation lithium arsenate and lithium trifluoromethanesulfonatelithium halideulmin acid lithiumchlorideetc. are illustratedand these one sort or two sorts or more can be used. Organic electrolysis liquid is prepared by dissolving an electrolyte in the above-mentioned solvent. It cannot be overemphasized that the solvent and electrolyte which are used when preparing an electrolysis solution are not limited to what was hung up above.
[0060]As an inorganic solid electrolytethey are mentioned by the nitride of Lia halogenidean oxygen acid saltthe phosphorus sulfide compoundetc.and more specificallyLi_3NLiILi_3N-LiI-LiOHL$iSiO_4$and $LiSiO_4$-LiI-LiOHLi_3PO_4-$Li_4SiO_4$$Li_2SiS_3$etc. are illustrated.
[0061]There are a substance which comprised a polymer which performs dissociation of the above-mentioned electrolyte and an electrolytea substance which gave the ionic dissociation group to the polymeretc. in an organic solid electrolyte. There are polymerphosphoric ester polymeretc. which contain polymerthe polypropylene oxide derivativeand this derivative containing a polyethylene oxide derivative and this derivative as a polymer which dissociates an electrolytefor example. The material which added polyacrylonitrile to the mixture of the polymer matrix material which made the above-mentioned aprotic polar solvent containpolymer containing an ionic dissociation groupand the above-mentioned aprotic polar solventand the electrolysis solution is also usable. It is also possible to use together an inorganic solid electrolyte and an organic solid electrolyte.
[0062]As a cathode in the lithium secondary battery of this inventionthe oxide which contains lithiumfor example can be used as positive active material in accordance with a conventional method. As a concrete example of positive active material$LiCoO_2$$LiNiO_2$$LiFeO_2$$LiMnO_2$$Li_xM_yN_zO_2$ that is these relative compounds (M here) [Fe and] . Are either Conickel and Mn and N expresses a transition metal4B group metalor 5B group metal. $LiMn_2O_4$ and $LiMn_{2-x}N_yO_4$ (here -- N -- a transition metal.) which is the relative compound $LiVO_2$ showing 4B group metal or 5B group metaletc. are mentioneddepending on a conducting materiala binderand the casea solid electrolyte etc. are mixed to thisand a cathode is formed in it. The mixture ratio of these each material can be used as about 5-50 weight sections of conducting materialsand about 1-30 weight sections of binders to active material 100 weight section. Especially as such a conducting materialit is not restrictedbut carbonsuch as publicly known carbon black (acetylene blackthermal blackchannel blacketc.)graphite powdermetal powderetc. can be usedand it is **. It is not limited in particular as a binderbut polyolefin system polymer; synthetic rubberssuch as fluorine system polymer; polyethylenesuch as publicly known polytetrafluoroethylene and polyvinylidene fluorideand polypropylenecan be used. The

loadings of a conducting material are smaller than five weight sectionsor since resistance or polarization of an electrodeetc. becomes large and service capacity becomes small when the loadings of a binder are larger than 30 weight sectionsa practical lithium secondary battery is unproducible. Since the amount of active materials contained in an electrode becomes less when there are more conducting materials than 50 weight sections (the relative rate changes according to the kind of conducting material to mix)the service capacity as a cathode becomes small. To binding capability being lost if a binder is smaller than one weight sectionif larger than 30 weight sectionsSince the amount of active materials contained in an electrode becomes less like the case of a conducting materialresistance or polarization of an electrodeetc. becomes large like a description further at the above and service capacity becomes smallit is not practical. In order to raise a binding property when producing a cathodeit is preferred to heat-treat at the temperature near the melting point of each binder.
[0063]As a separator for holding an electrolysis solutionthe Plastic solid of powdersuch as nonwoven fabricssuch as plastic fiber of publicly known electric insulationglass fiberand a natural fiberor textile fabricsand aluminaetc. are mentioned. Also in thesenonwoven fabrics which are synthetic resinssuch as polyethylene and polypropyleneare preferred from pointssuch as the stability of quality. When a cell carries out an abnormal heat generationa separator dissolves in the nonwoven fabric of these synthetic resins with heatthere are some which added the function which intercepts between a cathode and anodes in itand these can also be conveniently used for it from a viewpoint of safety. The thickness in particular of a separator is not limitedbut can hold the electrolysis solution of an initial complementand just prevents the short circuit of a cathode and an anodeis usually about 0.01-1 mmand is about 0.02-0.05 mm preferably.
[0064]Although the foil form of metalsuch as publicly known coppernickelstainless steelaluminumand titaniuma mesha porous bodyetc. are illustrated as a charge collectorit is not limited to these.
[0065]** ** In effect this inventiona carbon materialespecially the material of a high black lead system of crystallinity TarAfter being immersed in a Carboniferous system or petroleum system heavy oilsuch as a pitchetc. and separating the covered carbon material from heavy oil etc.the surface of the carbon material as a core material can obtain the new carbon material covered with heavy oil etc. by washing and drying with an organic solvent.
[0066]When the surface carbonizes the carbon material of a black lead system uniformly covered in the pitch at 600 ** - 2000 **a core material consists of material of a black lead system with a high degree of crystallinityand the surface can manufacture the carbon material of a unique structure where it is covered with the material of a carbon system with a low degree of crystallinity.
[0067]Since according to the manufacturing method of the invention in this application weld thru/or condensation of particles is not produced even when washingdesiccationand calcination are performed after covering the carbon material which is a core material with heavy oilsuch as a pitch and tarIt is not necessary to grind the obtained carbon materialand particles near what is called in the shape of ["that was able to take the angle"] a ball are obtained. The degradation factor of a material called mixing of the impurity accompanying grinding does not existeither.
[0068]In producing a nonaqueous secondary battery or a solid electrolyte cell using the

coating carbon material obtained by this inventionespecially the carbon material which covered the surface of the graphite material with those fired materialsuch as heavy oilit becomes possible to manufacture the cell excellent in both a charging and discharging characteristic and safety.

[0069]Inexpensive natural graphitean artificial graphiteetc. are used as a core materiala pitch inexpensive also as covering materialtaretc. are usedthe manufacturing method is also simple for this invention methodand since it is a manufacturing method which was dramatically excellent also in mass production natureit can obtain the inexpensive negative pole material for highly efficient lithium secondary batteries.

[0070]In this inventionthe combination of a core material and facingA low crystal carbon material + low crystal carbon materiala low crystal carbon material + quantity crystallinity carbon materialFour kinds of combination of a high crystallinity carbon material + low crystal carbon material and a high crystallinity carbon material + quantity crystallinity carbon material are possibleand if two more baking processes (carbonization calcination and graphitization calcination) are taken into considerationeight sorts of carbon materials will be obtained. Among thesethe high crystallinity carbon material + low crystal carbon material and high crystallinity carbon material + quantity crystallinity carbon material by which carbonization processing was carried outWhen using the carbon material which consists of combination of the high crystallinity carbon material + low crystal carbon material etc. by which conducting graphitization treatment was carried outreactivity with an electrolysis solution is lowand since the outstanding charging and discharging characteristic is demonstratedit is especially useful as a negative pole material for lithium secondary batteries.

[0071]A below form embodiment best [for inventing] explains invention concretely. Various kinds of measurement in each following embodiment was performed as follows.

1. The diameter of a centriole and particle size distribution of particles were measured using the "9220 micro of FRA(s) track" by measurement NIKKISO CO. LTD. of particle diameter.

2. About the carbon ingredient of the heavy oil origin which has covered a covering ratio and the circumference of a core material before measurement calcination of covering thickness. Solvent analysis was conducted according to the method specified to JIS K2425quinoline insoluble (%) was measuredand quinoline soluble (%) was computed by "100 - (quinoline insoluble)." The quantity of this quinoline soluble is the quantity of the carbon material for covering formation.

[0072]The weight ratio (covering ratio defined previously) of carbon material/for covering formation (carbon material for core material carbon material + covering formation) was computed by the above-mentioned method.

3. Specific surface area was measured using the "ASAP2400/nitrogen absorption BET specific surface area measuring device" by measurement Micromeritics of specific surface area.

4. True specific gravity was measured according to the method specified to measurement JIS R7212 of true specific gravity.

5. Method 55-63i.e.carbon material experimental technique 1 pp, that measurement of size (Lc, La) of microcrystal by measurement X-rays wide angle diffraction method of size of microcrystal by X ray wide angle diffraction method is publicly known It carried out by the method indicated toedited (technology company) by the Carbon Society of

Japan. The form factor K which asks for the size of microcrystal used 0.9.
6. The R value was calculated as a peak intensity ratio of $1360cm^{-1}/1580cm^{-1}$ from two peaks observed by the Raman spectrometry which used a 514.5-nm argon laser for the Raman spectrometry pan as a surface physical property of a carbon material.
7. It graphitized by dipping an anode in an electrolysis solution and calcinating the measuring pitch coating carbon material (pitch covering black lead) of the gas yield at the time of holding at an elevated temperature at 2800 ** among a nitrogen atmosphere for 1 hour. After mixing graphitization pitch covering black lead 95 weight section and PTFE("D-1" by DAIKIN INDUSTRIES LTD.) 5 dispersion type weight section and stirring uniformly by the liquid phaseit was made to dry and was considered as paste state. After molding this substance 0.25g for anodes with the pressing machine and producing a negative electrode body 2 cm in diametervacuum drying was carried out at 200 ** for 6 hours.
[0073]Subsequentlythis anode was charged until potential was set to 0V in the electrolysis solutionthe anode of the charging state was put into the beaker cell of 25 ml of electrolysis solutions which enteredit heated at 60 ** for 6 hoursand the gas yield of per graphitization pitch covering black lead 1g was measured.
[0074]As an electrolysis solutionthe mixed solvent (it is 3:3:4 at a volume ratio) of ethylene carbonatediethyl carbonateand methylpropionate in which $LiClO_4$ of $1moldm^{-3}$ was dissolved was used.
8. Production of a nonaqueous cell and the measurement cathode of a battery characteristic are generally produced by mixing a positive electrode materiala conducting materialand a binder. In this caseas a conducting materialmetallic materialssuch as carbon materialssuch as carbon black and black leador metal powderand metal wool yarnetc. are used suitably. Although it is also mixable with powdera binder may mix the thing which the solution was made to distributeand the dissolved thingin order to improve dispersibility more and to improve a binding property. When what was carried out in this wayand was distributed or dissolved in the solution is usedit is necessary to remove a solution by vacuum treatingheat treatmentor other means. It is also possible by furthermore heat-treating at the temperature near the melting point depending on the kind of binder to improve a binding property further.
[0075]$LiCoO_2$100 weight section was used for the positive electrode materialwhat mixed ten weight sections of PTFE powder by using acetylene black as a conducting material as ten weight sections and a binder was fabricated in working example in this application to an electrode 10 mm in diameterand the positive electrode body was obtained.
[0076]The negative electrode body was produced as follows by working example in this application.
[0077]Firstpitch covering black lead was calcinated at 1000 ** among a nitrogen atmosphere for 1 hourand it carbonized. After mixing this carbonization pitch covering black lead 95 weight section and PTFE("D-1" by DAIKIN INDUSTRIES LTD.) 5 dispersion type weight section and stirring uniformly by the liquid phaseit was made to dry and was considered as paste state. After molding 30 mg of this substance for anodes with the pressing machine and producing a negative electrode body 10 mm in diametervacuum drying was carried out at 200 ** for 6 hours.
[0078]Among a nitrogen atmosphereat 2800 **pitch covering black lead was calcinated for 1 hourand was graphitized. After mixing this graphitization pitch covering black lead

95 weight section and PTFE("D-1" by DAIKIN INDUSTRIES LTD.) 5 dispersion type weight section and stirring uniformly by the liquid phaseit was made to dry and was considered as paste state. After molding 30 mg of this substance for anodes with the pressing machine and producing a negative electrode body 10 mm in diametervacuum drying was carried out at 200 ** for 6 hours.
[0079]The polypropylene non-woven fabric was used as a separator.
[0080]When carbonization pitch covering black lead was used as a negative electrode bodythe propylene carbonate in which $LiClO_4$ of $1moldm^{-3}$ was dissolved was used for the electrolysis solution. When graphitization pitch covering black lead was usedthe mixed solvent (it is 3:3:4 at a volume ratio) of ethylene carbonatediethyl carbonateand methylpropionate in which $LiClO_4$ of $1moldm^{-3}$ was dissolved was used.
[0081]The discharge characteristic of the coin type lithium secondary battery produced using the positive electrode bodythe negative electrode bodyseparatorand electrolysis solution which were produced by performing it above was measured. Measurement was carried out under the constant current charge and discharge of 1 mA / $cm^2$and service capacity was made into capacity until cell voltage falls to 1.2V.
9. Both sides of 0.02-mm-thick copper foil were plastered with the paste state anode substance produced like the clauses (above-mentioned 8.) of production of a solid electrolyte celland production of the measurement nonaqueous cell of a battery characteristicand it driedand it rolled and was considered as a negative electrode plate 0.10 mm in thickness55 mm in widthand 90 mm in length.
[0082]Polyethylene oxide (molecular weight 600000) and $LiClO_4$ are dissolved in acetonitrileAfter casting this solution on a PTFE film (the "Teflon" by Du Pont) in the glove box of argon atmosphereit was neglected at 25 ** among the glove boxthe solvent was evaporatedit dried furtherand $_{(PFO)8}$ and $LiClO_4$ of the solid electrolyte were prepared.
[0083]The film mold lithium secondary battery was produced using $_{(PFO)8}$ and $LiClO_4$ as a solid electrolyte using $LiCoO_2$ as carbonization pitch covering black lead or graphitization pitch covering black leadsolid electrolyteand positive electrode body as a negative electrode body obtained above.
[0084]The discharge characteristic of the lithium secondary battery obtained above was measured. Measurement was carried out under the constant current charge and discharge of 1 mA / $cm^2$and service capacity was made into capacity until cell voltage falls to 1.2V. An embodiment 1 massive artificial graphite (diameter Dof centriole50=7.5micrometer and 0.1-150 micrometers of particle size distribution) d002=0.336nmLc=100nmLa = 97 nmspecific surface area =10.8m^2/gR value=0.26true-specific-gravity =2.25g /and cm^2 50gand the coal tar pitch of 80 ** of softening temperatures that removed primary QI beforehand (it and) [quinoline-insoluble-] 100 g of 30% toluene insoluble was put into a 500-ml SEPARERU flaskagitation mixing was carried out by 200 ** and ordinary pressure for 2 hoursand crude pitch covering black lead was obtained. After adding one copy of toluene to one copy of obtained crude pitch covering black lead and carrying out washing processing at 80 ** under churning for 1 hourit filtered and refined pitch covering black lead was obtained. It was 7.7 micrometers when the diameter D50 of a centriole of this refined pitch covering black lead was measured. Since the diameter D50 of a centriole of black lead as a core material was 7.5 micrometersthe thickness of a pitch layer is 0.1 micrometer.
[0085]The quinoline solublespecific surface areaand true specific gravity of the obtained

refined pitch covering black lead are shown in Table 1. Since the value of quinoline soluble is 9.6%the covering ratio of this refined pitch covering black lead is 0.096.
[0086]This refined pitch covering black lead was calcinated at 1000 ** among a nitrogen atmosphere for 1 hour (the heating rate of 25 ** / hr)and it carbonized. The specific surface area of the obtained carbonization pitch covering black leadtrue specific gravityan R valueand the volume reference integrated value of a particle of 1 micrometer or less are shown in Table 1. As a result of particle-size-distribution measurement of this refined pitch covering black leadhaving distribution in 0.1-150 micrometers like a core material was checkedand the X diffraction measurement result was the same as that of a core material. The carbonization pitch which forms an enveloping layer was understood that a degree of crystallinity is lower than a core material by comparison of the R value of a core material and carbonization pitch covering black lead. As a result of SEM observationthe artificial graphite which is a core material was covered with the carbonization pitch which forms an enveloping layerand it was checked that the edge part is round.
[0087]This carbonization pitch covering black lead was usedthe anode was producedand the nonaqueous secondary battery was produced using the propylene carbonate in which $LiClO_4$ of $1moldm^{-3}$ was dissolved as an electrolysis solution. The charge-and-discharge characteristic measurement result is shown in Table 2.
[0088]Carbonization pitch covering black lead was usedthe anode was producedand the solid electrolyte lithium secondary battery was produced. The charge-and-discharge characteristic measurement result is shown in Table 3.
The refined pitch covering black lead produced by making it be the same as that of embodiment 2 Embodiment 1 was calcinated at 1000 ** under the vacuum of 10torr for 1 hour (the heating rate of 25 ** / hr)and vacuum carbonization was carried out. The specific surface area of the obtained vacuum carbonization pitch covering black leadtrue specific gravityan R valueand the volume reference integrated value of a particle of 1 micrometer or less are combined with Table 1and are shown. As a result of particle-size-distribution measurement of this vacuum carbonization pitch covering black leadhaving distribution in 0.1-150 micrometers like a core material was checkedand the X diffraction measurement result was the same as that of a core material. The carbonization pitch which forms an enveloping layer was understood that a degree of crystallinity is lower than a core material by comparison of the R value of a core material and vacuum carbonization pitch covering black lead. As a result of SEM observationthe artificial graphite which is a core material was covered with the vacuum carbonization pitch which forms an enveloping layerand it was checked that the edge part is round.
[0089]The anode was produced using this vacuum carbonization pitch covering black leadand the nonaqueous secondary battery was produced using the propylene carbonate in which $LiClO_4$ of $1moldm^{-3}$ was dissolved as an electrolysis solution. The charge-and-discharge characteristic measurement result is combined with Table 2and is shown.
Among a nitrogen atmosphereat 2800 **the refined pitch covering black lead produced by making it be the same as that of embodiment 3 Embodiment 1 was calcinated for 1 hourand was graphitized. The specific surface area of the obtained graphitization pitch covering black leadtrue specific gravityan R valueand the volume reference integrated value of a particle of 1 micrometer or less are combined with Table 1and are shown. As a result of particle-size-distribution measurement of this graphitization pitch covering black

leadhaving distribution in 0.1-150 micrometers like a core material was checkedand the X diffraction measurement result was the same as that of a core material. The graphitization pitch which forms an enveloping layer was understood that a degree of crystallinity is lower than a core material by comparison of the R value of a core material and graphitization pitch covering black lead. As a result of SEM observationthe artificial graphite which is a core material was covered with the graphitization pitch which forms an enveloping layerand it was checked that the edge part is round.
[0090]The anode was produced using this graphitization pitch covering black leadand the nonaqueous secondary battery was produced using the mixed solvent (3:3:4) of ethylene carbonatediethyl carbonateand methylpropionate in which $LiClO_4$ of $1moldm^{-3}$ was dissolved as an electrolysis solution.
[0091]The gas yield in the inside of the electrolysis solution of this graphitization pitch covering black lead was measured. The charge-and-discharge characteristic measurement result and gas yield are combined with Table 2and are shown.
In the lead hammer furnace which can do very slow temperature upthe refined pitch covering black lead produced by making it be the same as that of embodiment 4 Embodiment 1 was calcinated at 1000 ** (below reducing atmospherethe heating rate of 5 ** / hr)and it carbonized. The specific surface area of this carbonization pitch covering black leadtrue specific gravityan R valueand the volume reference integrated value of a particle of 1 micrometer or less are combined with Table 1and are shown. As a result of particle-size-distribution measurement of this carbonization pitch covering black leadhaving distribution in 0.1-150 micrometers like a core material was checkedand the X diffraction measurement result was the same as that of a core material. The carbonization pitch which forms an enveloping layer was understood that a degree of crystallinity is lower than a core material by comparison of the R value of a core material and carbonization pitch covering black lead. As a result of SEM observationthe artificial graphite which is a core material was covered with the carbonization pitch which forms an enveloping layerand it was checked that the edge part is round.
[0092]The anode was produced using this carbonization pitch covering black leadand the nonaqueous secondary battery was produced using the propylene carbonate in which $LiClO_4$ of $1moldm^{-3}$ was dissolved as an electrolysis solution. A charge-and-discharge characteristic measurement result is combined with Table 2and is shown.
The refined pitch covering black lead produced by making it be the same as that of embodiment 5 Embodiment 1 was calcinated at 1300 ** among a nitrogen atmosphere for 1 hour (the heating rate of 25 ** / hr)and it carbonized. The specific surface area of this carbonization pitch covering black leadtrue specific gravityan R valueand the volume reference integrated value of a particle of 1 micrometer or less are combined with Table 1and are shown. As a result of particle-size-distribution measurement of this carbonization pitch covering black leadhaving distribution in 0.1-150 micrometers like a core material was checkedand the X diffraction measurement result was the same as that of a core material. The carbonization pitch which forms an enveloping layer was understood that a degree of crystallinity is lower than a core material by comparison of the R value of a core material and carbonization pitch covering black lead. As a result of SEM observationthe artificial graphite which is a core material was covered with the carbonization pitch which forms an enveloping layerand it was checked that the edge part is round.

[0093]The anode was produced using this carbonization pitch covering black leadand the nonaqueous secondary battery was produced using the propylene carbonate in which $LiClO_4$ of $1moldm^{-3}$ was dissolved as an electrolysis solution. The charge-and-discharge characteristic measurement result is combined with Table 2and is shown.
The refined pitch covering black lead produced by making it be the same as that of embodiment 6 Embodiment 1 was oxidized at 300 ** among an air atmosphere in the constant temperature/humidity chamber for 8 hours. The covering ratiospecific surface areaand true specific gravity of the obtained oxidation refined pitch covering black lead are shown in Table 1. This oxidation refined pitch covering black lead was calcinated at 1000 ** among a nitrogen atmosphere for 1 hour (the heating rate of 25 ** / hr)and it carbonized. The specific surface area of the obtained carbonization pitch covering black leadtrue specific gravityan R valueand the volume reference integrated value of a particle of 1 micrometer or less are combined with Table 1and are shown. As a result of particle-size-distribution measurement of this carbonization pitch covering black leadhaving distribution in 0.1-150 micrometers like a core material was checkedand the X diffraction measurement result was the same as that of a core material. The carbonization pitch which forms an enveloping layer was understood that a degree of crystallinity is lower than a core material by comparison of the R value of a core material and carbonization pitch covering black lead. As a result of SEM observationthe artificial graphite which is a core material was covered with the carbonization pitch which forms an enveloping layerand it was checked that the edge part is round.
[0094]The anode was produced using this carbonization pitch covering black leadand the nonaqueous secondary battery was produced using the propylene carbonate in which $LiClO_4$ of $1moldm^{-3}$ was dissolved as an electrolysis solution. The charge-and-discharge characteristic measurement result is combined with Table 2and is shown.
An embodiment 7 massive artificial graphite (diameter Dof centriole50=7.5micrometerparticle size distribution = 0.1-150 micrometers) d002=0.336nmLc=100nmLa = 97 nmspecific surface area =10.8m^2/gR value=0.26true-specific-gravity =2.25g /and cm^3 50gand the coal tar pitch of 80 ** of softening temperatures that removed primary QI beforehand (it and) [quinoline-insoluble-] 100 g of 30% toluene insoluble was put into a 500-ml SEPARERU flaskagitation mixing was carried out at 200 ** for 2 hoursand crude pitch covering black lead was obtained.
[0095]After adding one copy of toluene to one copy of obtained crude pitch covering black lead and carrying out washing processing at 20 ** under churning for 1 hourit filtered and refined pitch covering black lead was obtained. It was 7.9 micrometers when the diameter D50 of a centriole of this refined pitch covering black lead was measured. Since the diameter D50 of a centriole of the artificial graphite as a core material was 7.5 micrometersthe thickness of a pitch layer is 0.2 micrometer.
[0096]The covering ratiospecific surface areaand true specific gravity of the obtained refined pitch covering black lead are shown in Table 1. Since the value of quinoline soluble is 20.4%the covering ratio of this refined pitch covering black lead is 0.204.
[0097]The obtained refined pitch covering black lead was calcinated at 1000 ** among a nitrogen atmosphere for 1 hour (the heating rate of 25 ** / hr)and it carbonized. The specific surface area of this carbonization pitch covering black leadtrue specific gravityan R valueand the volume reference integrated value of a particle of 1 micrometer or less are combined with Table 1and are shown. As a result of particle-size-distribution

measurement of this carbonization pitch covering black leadhaving distribution in 0.1-150 micrometers like a core material was checkedand the X diffraction measurement result was the same as that of a core material. The carbonization pitch which forms an enveloping layer was understood that a degree of crystallinity is lower than a core material by comparison of the R value of a core material and carbonization pitch covering black lead. As a result of SEM observationthe artificial graphite which is a core material was covered with the carbonization pitch which forms an enveloping layerand it was checked that the edge part is round.

[0098]The anode was produced using this carbonization pitch covering black leadand the nonaqueous secondary battery was produced using the propylene carbonate in which $LiClO_4$ of 1moldm^{-3} was dissolved as an electrolysis solution. The charge-and-discharge characteristic measurement result is combined with Table 2and is shown.

Among a nitrogen atmosphereat 2800 **the refined pitch covering black lead produced by making it be the same as that of embodiment 8 Embodiment 7 was calcinated for 1 hourand was graphitized. The specific surface area of the obtained graphitization pitch covering black leadtrue specific gravityan R valueand the volume reference integrated value of a particle of 1 micrometer or less are combined with Table 1and are shown. As a result of particle-size-distribution measurement of this graphitization pitch covering black leadhaving distribution in 0.1-150 micrometers like a core material was checkedand the X diffraction measurement result was the same as that of a core material. The graphitization pitch which forms an enveloping layer was understood that a degree of crystallinity is lower than a core material by comparison of the R value of a core material and graphitization pitch covering black lead. As a result of SEM observationthe artificial graphite which is a core material was covered with the graphitization pitch which forms an enveloping layerand it was checked that the edge part is round.

[0099]The anode was produced using this graphitization pitch covering black leadand the nonaqueous secondary battery was produced using the mixed solvent (3:3:4) of ethylene carbonatediethyl carbonateand methylpropionate in which $LiClO_4$ of 1moldm^{-3} was dissolved as an electrolysis solution. The gas yield in the inside of the electrolysis solution of this graphitization pitch covering black lead was measured. The charge-and-discharge characteristic measurement result and gas yield are combined with Table 2and are shown.

An embodiment 9 massive artificial graphite (diameter Dof centriole50=7.5micrometerparticle size distribution = 0.1-150 micrometers) d002=0.336nmLc=100nmLa = 97 nmspecific surface area =10.8m^2/gR value=0.26true-specific-gravity =2.25g /and cm^3 50gand the coal tar pitch of 80 ** of softening temperatures that removed primary QI beforehand (it and) [quinoline-insoluble-] 100 g of 30% toluene insoluble was put into a 500-ml SEPARERU flaskagitation mixing was carried out at 200 ** for 2 hours under decompression (they are suction and decompression degree 50torr with a vacuum pump)and crude pitch covering black lead was obtained.

[0100]After adding one copy of toluene to one copy of obtained crude pitch covering black lead and carrying out washing processing at 80 ** under churning for 1 hourit filtered and refined pitch covering black lead was obtained. It was 7.7 micrometers when the diameter D50 of a centriole of this refined pitch covering black lead was measured. Since the diameter D50 of a centriole of the artificial graphite which is a core material

was 7.5 micrometersthe thickness of a pitch layer is 0.1 micrometer.
[0101]The covering ratiospecific surface areaand true specific gravity of this refined pitch covering black lead are shown in Table 1. Since the value of quinoline soluble is 10.4%the covering ratio of this refined pitch covering black lead is 0.104.
[0102]This refined pitch covering black lead was calcinated at 1000 ** among a nitrogen atmosphere for 1 hour (the heating rate of 25 ** / hr)and it carbonized. The specific surface area of the obtained carbonization pitch covering black leadtrue specific gravityan R valueand the volume reference integrated value of a particle of 1 micrometer or less are combined with Table 1and are shown. As a result of particle-size-distribution measurement of this graphitization pitch covering black leadhaving distribution in 0.1-150 micrometers like a core material was checkedand the X diffraction measurement result was the same as that of a core material. The graphitization pitch which forms an enveloping layer was understood that a degree of crystallinity is lower than a core material by comparison of the R value of a core material and graphitization pitch covering black lead. As a result of SEM observationthe artificial graphite which is a core material was covered with the graphitization pitch which forms an enveloping layerand it was checked that the edge part is round.
[0103]The anode was produced using this carbonization pitch covering black leadand the nonaqueous secondary battery was produced using the propylene carbonate in which $LiClO_4$ of $1moldm^{-3}$ was dissolved as an electrolysis solution. The charge-and-discharge characteristic measurement result is combined with Table 2and is shown.
An embodiment 10 massive artificial graphite (diameter Dof centriole50=7.5micrometerparticle size distribution = 0.1-150 micrometers) d002=0.336nmLc=100nmLa = 97 nmspecific surface area =$10.8m^2$/gR value=0.26true-specific-gravity =2.25g /and cm^3 50gand the coal tar pitch of 80 ** of softening temperatures that removed primary QI beforehand (it and) [quinoline-insoluble-] 100 g of 30% toluene insoluble was put into a 500-ml SEPARERU flaskagitation mixing was carried out at 200 ** for 2 hoursand crude pitch covering black lead was obtained.
[0104]After adding one copy of tar middle oil to one copy of obtained crude pitch covering black lead and carrying out washing processing at 20 ** under churning for 1 hourit filtered and refined pitch covering black lead was obtained. It was 7.6 micrometers when the diameter D50 of a centriole of this refined pitch covering black lead was measured. Since the diameter D50 of a centriole of black lead of a core material was 7.5 micrometersthe thickness of a pitch layer is 0.05 micrometer.
[0105]The covering ratiospecific surface areaand true specific gravity of this refined pitch covering black lead are shown in Table 1. Since the value of quinoline soluble is 8.8%the covering ratio of this refined pitch covering black lead is 0.088.
[0106]This refined pitch covering black lead was calcinated at 1000 ** among a nitrogen atmosphere for 1 hour (the heating rate of 25 ** / hr)and it carbonized. The specific surface area of this carbonization pitch covering black leadtrue specific gravityan R valueand the volume reference integrated value of a particle of 1 micrometer or less are combined with Table 1and are shown. As a result of particle-size-distribution measurement of this graphitization pitch covering black leadhaving distribution in 0.1-150 micrometers like a core material was checkedand the X diffraction measurement result was the same as that of a core material. The graphitization pitch which forms an enveloping layer was understood that a degree of crystallinity is lower than a core

material by comparison of the R value of a core material and graphitization pitch covering black lead. As a result of SEM observationthe artificial graphite which is a core material was covered with the graphitization pitch which forms an enveloping layerand it was checked that the edge part is round.

[0107]The anode was produced using this carbonization pitch covering black leadand the nonaqueous secondary battery was produced using the propylene carbonate in which $LiClO_4$ of $1moldm^{-3}$ was dissolved as an electrolysis solution. The charge-and-discharge characteristic measurement result is combined with Table 2and is shown.

An embodiment 11 massive artificial graphite (diameter Dof centriole50=7.5micrometerparticle size distribution = 0.1-150 micrometers) d002=0.336nmLc=100nmLa = 97 nmspecific surface area $=10.8m^2/g$R value=0.26true-specific-gravity =2.25g /and cm^3 50gand the coal tar pitch of 80 ** of softening temperatures that removed primary QI beforehand (it and) [quinoline-insoluble-] 200 g of 30% toluene insoluble was put into a 1000-ml SEPARERU flaskagitation mixing was carried out at 200 ** for 2 hoursand crude pitch covering black lead was obtained.

[0108]After adding one copy of toluene to one copy of obtained crude pitch covering black lead and carrying out washing processing at 80 ** under churning for 1 hourit filtered and refined pitch covering black lead was obtained. It was 7.9 micrometers when the diameter D50 of a centriole of this refined pitch covering black lead was measured. Since the diameter D50 of a centriole of black lead of a core material was 7.5 micrometersthe thickness of a pitch layer is 0.2 micrometer.

[0109]The covering ratiospecific surface areaand true specific gravity of this refined pitch covering black lead are shown in Table 1. Since the value of quinoline soluble is 17.3%the covering ratio is 0.173.

[0110]This refined pitch covering black lead was calcinated at 1000 ** among a nitrogen atmosphere for 1 hour (the heating rate of 25 ** / hr)and it carbonized. The specific surface area of this carbonization pitch covering black leadtrue specific gravityan R valueand the volume reference integrated value of a particle of 1 micrometer or less are combined with Table 1and are shown. As a result of particle-size-distribution measurement of this carbonization pitch covering black leadhaving distribution in 0.1-150 micrometers like a core material was checkedand the X diffraction measurement result was the same as that of a core material. The carbonization pitch which forms an enveloping layer was understood that a degree of crystallinity is lower than a core material by comparison of the R value of a core material and carbonization pitch covering black lead. As a result of SEM observationthe artificial graphite which is a core material was covered with the carbonization pitch which forms an enveloping layerand it was checked that the edge part is round.

[0111]The anode was produced using this carbonization pitch covering black leadand the nonaqueous secondary battery was produced using the propylene carbonate in which $LiClO_4$ of $1moldm^{-3}$ was dissolved as an electrolysis solution. The charge-and-discharge characteristic measurement result is combined with Table 2and is shown.

An embodiment 12 massive artificial graphite (diameter Dof centriole50=7.5micrometerparticle size distribution = 0.1-150 micrometers) d002=0.336nmLc=100nmLa = 97 nmspecific surface area $=10.8m^2/g$The coal tar pitch of 80 ** of softening temperatures which has not removed R value=0.26true-specific-gravity =2.25g /and cm^3 50gand primary QI (3.9% of quinoline insoluble) 100 g of 34%

toluene insoluble was put into a 500-ml SEPARERU flaskagitation mixing was carried out at 200 ** under ordinary pressure for 2 hoursand crude pitch covering black lead was obtained.

[0112]After adding one copy of toluene to one copy of obtained crude pitch covering black lead and carrying out washing processing at 80 ** under churning for 1 hourit filtered and refined pitch covering black lead was obtained. It was 7.9 micrometers when the diameter D50 of a centriole of this refined pitch covering black lead was measured. Since the diameter D50 of a centriole of black lead of a core material was 7.5 micrometersthe thickness of a pitch layer is 0.2 micrometer.

[0113]The covering ratio of this refined pitch covering black leadspecific surface areaand true specific gravity are shown in Table 1. Since the value of quinoline soluble is 7.5%a covering ratio is 0.075.

[0114]This refined pitch covering black lead was calcinated at 1000 ** among a nitrogen atmosphere for 1 hour (the heating rate of 25 ** / hr)and it carbonized. The specific surface area of this carbonization pitch covering black leadtrue specific gravityan R valueand the volume reference integrated value of a particle of 1 micrometer or less are combined with Table 1and are shown. As a result of particle-size-distribution measurement of this carbonization pitch covering black leadhaving distribution in 0.1-150 micrometers like a core material was checkedand the X diffraction measurement result was the same as that of a core material. The carbonization pitch which forms an enveloping layer was understood that a degree of crystallinity is lower than a core material by comparison of the R value of a core material and carbonization pitch covering black lead. As a result of SEM observationthe artificial graphite which is a core material was covered with the carbonization pitch which forms an enveloping layerand it was checked that the edge part is round.

[0115]The anode was produced using this carbonization pitch covering black leadand the nonaqueous secondary battery was produced using the propylene carbonate in which $LiClO_4$ of $1moldm^{-3}$ was dissolved as an electrolysis solution. The charge-and-discharge characteristic measurement result is combined with Table 2and is shown.

An embodiment 13 massive artificial graphite (diameter Dof centriole50=7.5micrometerparticle size distribution = 0.1-150 micrometers) d002=0.336nmLc=100nmLa = 97 nmspecific surface area =10.8m^2/gR value=0.26true-specific-gravity =2.25g /and cm^3 50gand coal tar of 10 ** of softening temperatures from which primary QI was removed beforehand (it and) [quinoline-insoluble-] 100 g of 8% toluene insoluble was put into a 500-ml SEPARERU flaskagitation mixing was carried out at 200 ** under ordinary pressure for 2 hoursand crude pitch covering black lead was obtained.

[0116]After adding one copy of toluene to one copy of obtained crude pitch covering black lead and carrying out washing processing at 80 ** under churning for 1 hourit filtered and refined pitch covering black lead was obtained. It was 7.6 micrometers when the diameter D50 of a centriole of this refined pitch covering black lead was measured. Since the diameter D50 of a centriole of black lead of a core material was 7.5 micrometersthe thickness of a pitch layer is 0.05 micrometer.

[0117]The covering ratiospecific surface areaand true specific gravity of the obtained refined pitch covering black lead are combined with Table 1and are shown. Since the measured value of quinoline soluble is 7.8%the covering ratio of this refined pitch

covering black lead is 0.078.
[0118]This refined pitch covering black lead was calcinated at 1000 ** among a nitrogen atmosphere for 1 hour (the heating rate of 25 ** / hr)and it carbonized. The specific surface area of this carbonization pitch covering black leadtrue specific gravityan R valueand the volume reference integrated value of a particle of 1 micrometer or less are combined with Table 1and are shown. As a result of particle-size-distribution measurement of this carbonization pitch covering black leadhaving distribution in 0.1-150 micrometers like a core material was checkedand the X diffraction measurement result was the same as that of a core material. The carbonization pitch which forms an enveloping layer was understood that a degree of crystallinity is lower than a core material by comparison of the R value of a core material and carbonization pitch covering black lead. As a result of SEM observationthe artificial graphite which is a core material was covered with the carbonization pitch which forms an enveloping layerand it was checked that the edge part is round.
[0119]The anode was produced using this carbonization pitch covering black leadand the nonaqueous secondary battery was produced using the propylene carbonate in which $LiClO_4$ of $1moldm^{-3}$ was dissolved as an electrolysis solution. The charge-and-discharge characteristic measurement result is combined with Table 2and is shown.
[0120]The anode was produced using carbonization pitch covering black leadandsubsequently the solid electrolyte lithium secondary battery was produced. The charge-and-discharge characteristic measurement result is combined with Table 3and is shown.
Embodiment 14 -- a spherical meso-carbon-micro-beads graphitization article ("MCMB-6-28" by Osaka Gas Co.Ltd..) Diameter Dof centriole50=6.0mmparticle size distribution = 0.1-50 micrometers d 002= 0.336 nmLc=50nmLa = 90 nmspecific surface area $=3.0m^2/gR$ value=0.42true-specific-gravity =2.20g /and cm^3 50gand the coal tar pitch of 80 ** of softening temperatures that removed primary QI beforehand (it and) [quinoline-insoluble-] 100 g of 30% toluene insoluble was put into a 500-ml SEPARERU flaskagitation mixing was carried out at 200 ** under ordinary pressure for 2 hoursand the crude pitch covering meso-carbon-micro-beads graphitization article was obtained.
[0121]After adding one copy of toluene to one copy of obtained crude pitch covering meso-carbon-micro-beads graphitization article and carrying out washing processing at 80 ** under churning for 1 hourit filtered and the refined pitch covering meso-carbon-micro-beads graphitization article was obtained. It was 6.2 micrometers when the diameter D50 of a centriole of this refined pitch covering meso-carbon-micro-beads graphitization article was measured. Since the diameter D50 of a centriole of black lead as a core material was 6.0 micrometersthe thickness of a pitch layer is 0.1 micrometer.
[0122]The covering ratiospecific surface areaand true specific gravity of this refined pitch covering meso-carbon-micro-beads graphitization article are shown in Table 1. Since the value of quinoline soluble is 9.8%a covering ratio is 0.098.
[0123]This refined pitch covering meso-carbon-micro-beads graphitization article was calcinated at 1000 ** among a nitrogen atmosphere for 1 hour (the heating rate of 25 ** / hr)and it carbonized. The specific surface area of this carbonization pitch covering meso-carbon-micro-beads graphitization articletrue specific gravityan R valueand the volume reference integrated value of a particle of 1 micrometer or less are combined with Table 1and are shown. Having distribution in 0.1-50 micrometers like a core material was

checked as a result of particle-size-distribution measurement of this carbonization pitch covering meso-carbon-micro-beads graphitization article. The carbonization pitch which forms an enveloping layer was understood that a degree of crystallinity is lower than a core material by comparison of the R value of a core material and a carbonization pitch covering meso-carbon-micro-beads graphitization article.
[0124]The anode was produced using this carbonization pitch covering meso-carbon-micro-beads graphitization articleand the nonaqueous secondary battery was produced using the propylene carbonate in which $LiClO_4$ of 1 moldm^{-3} was dissolved as an electrolysis solution. The charge-and-discharge characteristic measurement result is shown in Table 2.
An embodiment 15 massive artificial graphite (diameter Dof centriole50=16.2micrometer and 0.1-120 micrometers of particle size distribution) d002=0.337nmLc=100nmLa = 71 nmspecific surface area =14.4m^2/gR value=0.31the true specific gravity of 1.96g / cm^3 50gand the coal tar pitch of 80 ** of softening temperatures that removed primary QI beforehand (it and) [quinoline-insoluble-] 100 g of 30% toluene insoluble was put into a 1000-ml SEPARERU flaskagitation mixing was carried out by 250 ** ordinary pressure for 5 hoursand crude pitch covering black lead was obtained.
[0125]After adding three copies of toluene to one copy of obtained crude pitch covering black lead and carrying out washing processing at 50 ** under churning for 5 hoursit filtered and refined pitch covering black lead was obtained. It was 16.6 micrometers when the diameter D50 of a centriole of this refined pitch covering black lead was measured. Since the diameter D50 of a centriole of black lead as a core material was 16.2 micrometersthe thickness of a pitch layer is 0.2 micrometer.
[0126]The covering ratio of the obtained refined pitch covering black leadspecific surface areaand true specific gravity are shown in Table 1. Since the measured value of quinoline soluble is 11.3%the covering ratio of the carbon material for covering formation is 0.113.
[0127]This refined pitch covering black lead was calcinated at 1000 ** among a nitrogen atmosphere for 1 hour (the heating rate of 25 ** / hr)and it carbonized. The specific surface area of the obtained carbonization pitch covering black leadtrue specific gravityan R valueand the volume reference integrated value of a particle of 1 micrometer or less are shown in Table 1. As a result of particle-size-distribution measurementit has distribution in 0.1-120 micrometersand the X diffraction measurement result was the same as that of a core material. By comparison of the R value of a core material and carbonization pitch covering black leadthe carbonization pitch which is a carbon material for covering formation was understood that a degree of crystallinity is lower than a core material. As a result of SEM observationthe artificial graphite of the core material was covered with the carbonization pitch which is a carbon material for covering formationand it was checked that the edge part is round.
[0128]This carbonization pitch covering black lead was usedthe anode was producedand the nonaqueous secondary battery was produced using the propylene carbonate in which $LiClO_4$ of 1moldm^{-3} was dissolved as an electrolysis solution. The charge-and-discharge characteristic measurement result is shown in Table 2.
An embodiment 16 massive artificial graphite (diameter Dof centriole50=16.2micrometer and 1-80 micrometers of particle size distribution) d002=0.338nmLc=83nmLa = 63 nmspecific surface area =6.8m^2/gR value=0.38the true specific gravity of 2.02g / cm^3 50gand the coal tar pitch of 80 ** of softening temperatures that removed primary QI

beforehand (it and) [quinoline-insoluble-] 100 g of 30% toluene insoluble was put into a 1000-ml SEPARERU flaskagitation mixing was carried out by 250 ** ordinary pressure for 5 hoursand crude pitch covering black lead was obtained. After adding three copies of toluene to one copy of obtained crude pitch covering black lead and carrying out washing processing at 50 ** under churning for 5 hoursit filtered and refined pitch covering black lead was obtained. It was 12.0 micrometers when the diameter D50 of a centriole of this refined pitch covering black lead was measured. Since the diameter D50 of a centriole of black lead as a core material was 11.6 micrometersthe thickness of a pitch layer is 0.2 micrometer.
[0129]The covering ratio of the obtained refined pitch covering black leadspecific surface areaand true specific gravity are shown in Table 1. Since the measured value of quinoline soluble is 12.3%a covering ratio is 0.123.
[0130]This refined pitch covering black lead was calcinated at 1000 ** among a nitrogen atmosphere for 1 hour (the heating rate of 25 ** / hr)and it carbonized. The specific surface area of the obtained carbonization pitch covering black leadtrue specific gravityan R valueand the volume reference integrated value of a particle of 1 micrometer or less are shown in Table 1. As a result of particle-size-distribution measurementit has distribution in 1-80 micrometersand the X diffraction measurement result was the same as that of a core material. By comparison of the R value of a core material and carbonization pitch covering black leadthe carbonization pitch which is a carbon material for covering formation was understood that a degree of crystallinity is lower than a core material. As a result of SEM observationthe artificial graphite of the core material was covered with the carbonization pitch which is a carbon material for covering formationand it was checked that the edge part is round.
[0131]This carbonization pitch covering black lead was usedthe anode was producedand the nonaqueous secondary battery was produced using the propylene carbonate in which $LiClO_4$ of $1moldm^{-3}$ was dissolved as an electrolysis solution. The charge-and-discharge characteristic measurement result is shown in Table 2.
Embodiment 17 scale-like artificial graphite (diameter Dof centriole50=18.9micrometer and 0.1-150 micrometers of particle size distribution) d002=0.340nmLc=42nmLa = 50 nmspecific surface area $=9.2m^2/g$R value=0.49the true specific gravity of $1.82g / cm^3$ 50gand the coal tar pitch of 80 ** of softening temperatures that removed primary QI beforehand (it and) [quinoline-insoluble-] 100 g of 30% toluene insoluble was put into a 1000-ml SEPARERU flaskagitation mixing was carried out by 250 ** ordinary pressure for 5 hoursand crude pitch covering black lead was obtained. After adding three copies of toluene to one copy of obtained crude pitch covering black lead and carrying out washing processing at 50 ** under churning for 5 hoursit filtered and refined pitch covering black lead was obtained. It was 19.3 micrometers when the diameter D50 of a centriole of this refined pitch covering black lead was measured. Since the diameter D50 of a centriole of black lead as a core material was 18.9 micrometersthe thickness of a pitch layer is 0.2 micrometer.
[0132]The covering ratio of the obtained refined pitch covering black leadspecific surface areaand true specific gravity are shown in Table 1. Since the measured value of quinoline soluble is 10.6%a covering ratio is 0.106.
[0133]This refined pitch covering black lead was calcinated at 1000 ** among a nitrogen atmosphere for 1 hour (the heating rate of 25 ** / hr)and it carbonized. The specific

surface area of the obtained carbonization pitch covering black leadtrue specific gravityan R valueand the volume reference integrated value of a particle of 1 micrometer or less are shown in Table 1. As a result of particle-size-distribution measurementit has distribution in 0.1-150 micrometersand the X diffraction measurement result was the same as that of a core material. By comparison of the R value of a core material and carbonization pitch covering black leadthe carbonization pitch which is a carbon material for covering formation was understood that a degree of crystallinity is lower than a core material. As a result of SEM observationthe artificial graphite of the core material was covered with the carbonization pitch which is a carbon material for covering formationand it was checked that the edge part is round.

[0134]This carbonization pitch covering black lead was usedthe anode was producedand the nonaqueous secondary battery was produced using the propylene carbonate in which $LiClO_4$ of $1moldm^{-3}$ was dissolved as an electrolysis solution. The charge-and-discharge characteristic measurement result is shown in Table 2.

the artificial graphite (the diameter D of a centriole -- 50= 23.8 micrometers) of embodiment 18 whisker shape 0.1-150 micrometers of particle-size-distribution d 002= 0.347 nmLc = 25 nmLa = 15 nmspecific surface area =$13.5m^2/g$R value=0.68true-specific-gravity 1.60 $g/cm^3$50g and the coal tar pitch of 80 ** of softening temperatures which removed primary QI beforehand (it and) [quinoline-insoluble-] 100 g of 30% toluene insoluble was put into a 1000-ml SEPARERU flaskagitation mixing was carried out by 250 ** ordinary pressure for 5 hoursand crude pitch covering black lead was obtained. After adding three copies of toluene to one copy of obtained crude pitch covering black lead and carrying out washing processing at 50 ** under churning for 5 hoursit filtered and refined pitch covering black lead was obtained. It was 24.2 micrometers when the diameter D50 of a centriole of this refined pitch covering black lead was measured. Since the diameter D50 of a centriole of black lead as a core material was 23.8 micrometersthe thickness of a pitch layer is 0.2 micrometer.